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Nanocluster dynamics in fast rate epitaxy under mesoplasma condition

L.W. Chen *, Y. Shibuta, M. Kambara, T. Yoshida

Department of Materials Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

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ABSTRACT

The dynamics of Si nano-clusters during epitaxial growth has been investigated with molecular dynamics simulation using the Tersoff potential. Several nm sized Si cluster formed during rapid cooling was found to deform instantaneously upon impingement on a Si(100) substrate at the same time with the spontaneous ordering of the atomic structure to that of the substrate. Due to the increased fraction of high-energy atoms at the surface, smaller clusters (~1 nm) are favorable for such a deformation even at lower temperatures. This is the advantage of loosely-bound cluster as growth precursor to attain epitaxy with reduced impact energies.

1. Introduction

For the last decade, considerable efforts have been devoted to the exploration and development of Si film photovoltaic (PV) cells. Among various thin film forms of Si PV cells, single crystalline Si (sc-Si) as active layer is promising due to its long-term stability and high conversion efficiency (~25%) compared to that of micro-crystalline (~13%) or polycrystalline (~17%) structures [1]. From the processing point of view, high rate and large area epitaxial deposition techniques are to be established to realize sc-Si thin films. In this regard, we have proposed that the cluster formation due to strong thermophoresis originating from the steep temperature gradient ahead of the substrate is one of the important features for high rate deposition [2–4]. In fact, we have shown that the growth and transport of Si cluster in the thermal boundary layer between the plasma and substrate have strong correlation with deposition rate as well as film structure by demonstrating homoepitaxial Si film deposition at a rate of ~33 nm/s with mesoplasma chemical vapor deposition [5,6]. Uniqueness of this process have been identified experimentally by the *in situ* X-ray scattering measurement to be the formation of 2–3 nm Si clusters having loosely-bound atomic structure as growth precursors within the thermal boundary layer region ahead of the film growth surface [7–9].

In our previous study [10], the condensation process during continuous cooling from high temperature Si vapors was simulated by molecular dynamics (MD) simulation utilizing the Lennard–Jones (LJ) potential, and the formation of globular clusters having liquid-like structure of around 2–3 nm in size, different from that of gas or solid phase, was identified. Furthermore, the dynamics of such clusters as growth precursors on single crystalline substrate during epitaxial growth was investigated. For the case of the clusters with 5–6 nm in size, upon impingement on a substrate, atoms of the cluster are found to be aligned partially to follow the substrate only in the vicinity of the substrate/cluster interface. In contrast, all of the constituent Si atoms of the 2–3 nm sized clusters are ordered instantaneously and spontaneously to the structure of the substrate. This suggests that rapid atomic self-ordering of the cluster is one of the keys to facilitate the fast rate epitaxy.

Several groups have also reported the MD simulation of the cluster impingement on substrate to identify the necessary condition for the epitaxial growth [11–14]. Biswas et al. [11] and Kwon et al. [12] studied the impact of a 33-atom amorphous Si cluster with the kinetic energy of 2.1 eV/atom onto Si(111) substrate and found that epitaxial growth was achieved when high surface diffusion is attained. Xie et al. [13] investigated the impingement of a 10-atom Si cluster having glassy structure at the impact energy of larger than 2 eV/atom on a Si(111) substrate, and pointed out that spreading of the deposited clusters and high surface diffusion of atoms are both necessary to attain epitaxy. Tarus et al. [14] studied the deposition of Si_{20} cluster at the ground state on a Si(001) substrate, and found the rearrangement of atoms after complete deformation of Si_{20} fullerene at a high impact energy of 5 eV/atom. All of these epitaxial growth mechanisms are more or less based on the deformation of clusters due to high kinetic (impact) energies and the subsequent fast diffusion of atoms on surface. This is somewhat different from the epitaxial dynamics of the loosely-bond cluster as growth precursor at low impact energy, simulated by the LJ potential, under the mesoplasma condition [10].

In the present Letter, therefore, using the Tersoff many-body model potential that may be more appropriate to describe the covalently bonded condensed systems, we have attempted MD simulation to elucidate detailed cluster characteristics and its dynamics in condensation/film formation. The mechanism of fast rate epitaxial growth through a low energy impact of cluster growth precursors is then discussed.

* Corresponding author.
E-mail address: chenwen@plasma.t.u-tokyo.ac.jp (L.W. Chen).

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2. Simulation methodology

MD simulation for the Si cluster formation and the interaction between cluster and Si(100) substrate was carried out with the Tersoff potential [15,16] that has been used to calculate the Si system. Although it gives higher Si melting temperature (T_m) around 2500 K than the experimental results of 1687 K [17], Motooka and Munetoh [18] have shown that it can well reproduce structural properties of crystalline Si. Therefore, we consider that it is at least meaningful to describe the change in the transformation of Si structure with the relative temperature to the melting point.

Initially, 1000 Si atoms were placed in a MD cell of $100 \times 100 \times 100$ Å, and heated up immediately to 1.78 T_m. It was then cooled down to 0.18 T_m at a rate of 2.7×10^{12} K/s, and the clustering of atoms during continuous cooling was analyzed. The formed Si cluster that consists of n Si atoms is denoted hereafter as Si_n. These clusters were then used as the growth precursor for the cluster impingement simulation. The area for impingement was set to be 32.59×32.59 Å having five atomic planes of the Si(100) structure. The bottom two atomic layers were fixed and the top three atomic layers near the surface were assigned as movable thermal control layers, acting as an ideal heat reservoir to maintain a constant substrate temperature. The velocities of the atoms in the thermal layers were rescaled at each time step of the simulation according to the substrate temperature. The temperature of the system was controlled by the velocity scaling method. Periodic boundary condition was applied to all the faces of the square MD cells for the cluster formation, and also to four walls normal to the bottom Si substrate for the impingement calculation. The time step used in all simulations was chosen to be 0.5 fs. Most importantly, no extra impact energy was applied to the cluster, because the growth precursor in the actual experiment was considered to arrive at the growth front at a group velocity of several 10 m/s, which was somewhat 'soft-landed' on the surface [19]. Therefore, the cluster was set 10 Å above the substrate surface and falls downward to the substrate with the translational kinetic energy of $\sim 1.2 \times 10^{-3}$ eV/atom.

Furthermore, in order to identify more actual dynamics of the clusters as growth precursors in the epitaxial deposition situation, 20 of Si_{35} and 5 Si_{181} clusters were impinged one after another on the film growth surface, and the multiple interactions between the clusters were simulated. The position of the impact is selected randomly to avoid the artificial interaction at each cluster impact.

3. Results and discussion

3.1. Cluster deformation during epitaxial ordering

The inset of Figure 1 summarizes the temperature variation of the radial distribution function (RDF) of the Si cluster having 216 Si atoms, created during rapid cooling. It is seen that, at temperature higher than 1.77 T_m, atoms are considered to be at the gas phase because the second-nearest neighbor peak, I_2, is not clearly identified (the weak first-nearest neighbor peak, I_1, is due to the finite MD cell size). As temperature decreases below T_m, I_2 starts to appear and also I_1 becomes sharper, suggesting the formation of the condensed phase. Representing the temperature variation of the ordering of the Si atomic structure, the relative intensity of I_2/I_1 was plotted in Figure 1. While I_2/I_1 is nearly 0 at high temperature, representing the gas phase, it abruptly increases to 0.4–0.6 as temperature reaches around 1.7 T_m, due to I_2 appears. However, it shows a gradual decrease to 0.2–0.3 as temperature decreases lower than T_m, because the intensity of I_1 becomes larger. It is therefore at least understood from this tendency that clusters created as liquid-like nuclei just after condensation followed by the

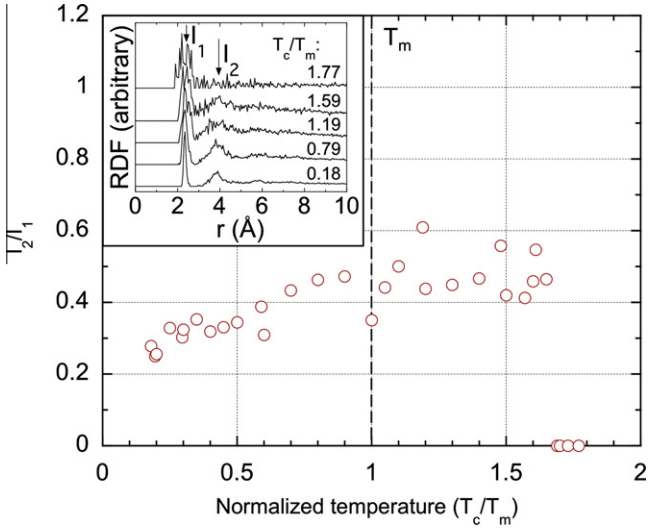

Figure 1. Change in the I_2/I_1 of the RDF for 216 Si atoms during cooling from 1.78 T_m to 0.18 T_m at a rate of 2.7×10^{12} K/s. Inset: radial distribution function (RDF).

change to solid phase as temperature decreases. Furthermore, the RDF obtained as in Figure 1 is totally different from that of the Si solid in terms of the sharpness of the peaks and also of the absence of high order nearest neighbor peaks. Therefore, the structure of the nuclei cluster should be characterized by liquid-like structure, different from solid or vapor, forming as a meta-stable phase. In fact, if one assumes that the boiling point, T_b, of the Tersoff potential is represented roughly by the relative magnitude of the actual T_b/T_m of Si, T_b for Tersoff would become ~ 2 T_m. Comparison of T_b and T_m with the temperature at the steep increase in I_2/I_1 therefore suggests that nucleation occurs at least above the melting point and possibly at around or below the boiling point. As important as its structural characteristics, similar RDF spectrum was fundamentally obtained for the clusters with different sizes ranging at least from 1 to 5 nm.

The clusters created as in Figure 1 were then used for the simulation of the cluster impingement on the substrate. Figure 2a shows the change in the structure of Si_{216} cluster with various initial cluster temperatures (T_c) after impingement onto Si(100) substrate at different substrate temperatures (T_s). At 0.59 T_m, Si_{216} cluster deforms only locally at the position of the impact and the rest part of the cluster remains its original globular shape, roughly independent of T_c. When T_s increased to 0.69 T_m, the cluster shape is seen to change from an overall globular shape to a mound-like structure upon impact. Although it is only in the vicinity of the impact interface, alignment of the atoms of the cluster to the crystal structure of the substrate is observed at this temperature. At T_s higher than 0.79 T_m, rearrangement of the atoms is clearly seen for almost of all the atoms within the cluster, possibly because they obtain enough energy to move from substrate at high temperature.

These self-ordering of atoms are quantified by counting the number of Si atoms as a function of distance from the substrate surface and summarized in Figure 2b for the case of the impingement of Si_{216} with $T_c = 0.79$ T_m onto the substrate at different T_s. At $T_s = 0.59$ T_m, the atoms are distributed nearly uniformly within the cluster. However, when T_s increases to 0.69 T_m, the atoms start to get aligned with an interval of around 0.14 nm that corresponds to the distance between the nearest crystal planes along the [100] direction in the Si unit cell. As T_s increases further to 0.79 T_m, such an alignment of Si atoms is more clearly observed as layers especially near the substrate. Eventually, when T_s reaches 0.89 T_m, the number of layers decreases while the number of Si atoms in each layer increases, which indicates that the cluster deforms